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14. ABSTRACT
The objectives of this project were to (1) develop optimization methodology for generating the coordinate space trajectories of molecules that are undergoing conformational transformations as a result of light-induced excitations and subsequent relaxation processes and (2) develop the principal investigator's Wigner-Poisson code and extend that code to deal with longer devices and more complex barrier profiles. Over the course of the project we have produced a code for (1) using sparse interpolation and applied that code to several molecules. We have a new C++ code for (2) and have used that code for grid refinement, discretization, stability, and bifurcation studies

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Report Title

ABSTRACT

The objectives of this project were to (1) develop optimization methodology for generating the coordinate space trajectories of molecules that are undergoing conformational transformations as a result of light-induced excitations and subsequent relaxation processes and (2) develop the principal investigator's Wigner-Poisson code and extend that code to deal with longer devices and more complex barrier profiles. Over the course of the project we have produced a code for (1) using sparse interpolation and applied that code to several molecules. We have a new C++ code for (2) and have used that code for grid refinement, discretization, stability, and bifurcation studies.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
07/05/2012	15.00	David Mokrauer, C. T. Kelley. Sparse interpolatory reduced-order models for simulation of light-induced molecular transformations, Optimization Methods and Software, (07 2012): 0. doi: 10.1080/10556788.2012.693928
07/25/2011	8.00	David Mokrauer, C. T. Kelley, Alexei Bykhovski. Efficient Parallel Computation of Molecular Potential Energy Surfaces for the Study of Light-Induced Transition Dynamics in Multiple Coordinates, IEEE Transactions on Nanotechnology, (01 2011): . doi: 10.1109/TNANO.2010.2058862
07/27/2011	10.00	I. C. F. Ipsen, C. T. Kelley, S. R. Pope. RANK-DEFICIENT NONLINEAR LEAST SQUARES PROBLEMS AND SUBSET SELECTION, Society for Industrial and Applied Mathematics, (03 2011): 0. doi:
07/27/2011	11.00	C. T. Kelley. Implicit Filtering, IEEE Transactions on Nanotechnology, (08 2011): 0. doi:
08/04/2011	9.00	Anne S. Costolanski, C. T. Kelley. Efficient Solution of the Wigner–Poisson Equations for Modeling Resonant Tunneling Diodes, IEEE Transactions on Nanotechnology, (11 2010): 0. doi: 10.1109/TNANO.2010.2053214
12/22/2013	18.00	C. T. Kelley, Li-Zhi Liao, Liqun Qi, Moody T. Chu, J. P. Reese, C. Winton. Projected Pseudotransient Continuation, SIAM Journal on Numerical Analysis, (01 2008): 0. doi: 10.1137/07069866X
TOTAL:		**6**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper
05/01/2013 17.00	Alex Toth, C. T. Kelley. Convergence Analysis for Anderson Acceleration, SIAM J Numer Anal, (05 2013): 0. doi:
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Number of Papers published in non peer-reviewed journals:

(c) Presentations

A. Costolanski, ``An Efficient Parallel Solution to the Wigner-Poisson
Equations, High Performance Computing Symposium (HPC 2013), San Diego, CA,
April 2013.

C. T. Kelley, ``Newton's Method for Monte Carlo Based Residuals", CUNY Applied Mathematics Symposium, New York, NY. April 25, 2013.

C. T. Kelley, ``Randomized nonlinear equations in neutronics", October 19–22, 2012. Eleventh International Symposium on Distributed Computing and Applications to Business, Engineering and Science, Guilin, China. Colloquium and Seminar Talks

C. T. Kelley, ``Newton's Method for Monte Carlo Based Residuals", 12th International Symposium on Distributed Computing and Applications to Business, Engineering and Science, London, England, Sept 2—4, 2013. Keynote address.

C. T. Kelley, ``Optimization for Quantum Chemistry", Second Conference on Engineering and Computational Mathematics, Hong Kong Polytechnic University, Hong Kong, China, Dec 16-18, 2013.

Anne Costolanski and C. T. Kelley
"Parallel Implementation of the Wigner Poisson Formulation for Modeling
Resonant Tunneling Diodes" (Poster)
2011 NANO-DDS Conference, New York, New York, Aug 29-Sep 1, 2011.

C. T. Kelley and D. Mokrauer
"Multi-dimensional sparse surrogate models for determining light-induced
effects on molecular conformations" (Poster)
2011 NANO-DDS Conference, New York, New York, Aug 29-Sep 1, 2011.

C. T. Kelley and D. Mokrauer
"Sparse interpolatory reduced-order models for simulation of
light-induced molecular transformations",
8th International Conference on Numerical Optimization and Numerical
Linear Algebra, Xia Men, China, November, 2011.

C. T. Kelley and D. Mokrauer "Sparse interpolatory reduced-order models for simulation of light-induced molecular transformations", 8th International Conference on Numerical Optimization and Numerical Linear Algebra, Xia Men, China, November, 2011.
C. T. Kelley and D. Mokrauer, "Sparse interpolatory reduced-order models for simulation of light-induced molecular transformations", Minisymposium on Reduced-Order Models, SIAM Conference on Uncertainty Quantification, Raleigh, NC, April 2012.
C. T. Kelley and D. Mokrauer, "Interpolatory reduced order models for molecular dynamics" International Symposiumon Mathematical Programming, Berlin, Germany, August 19–24, 2012.

C. T. Kelley, "Rank-Deficient Nonlinear Least Squares Problems",
IFIP Working Group 2.5 Symposium, Raleigh, NC, September 2009

C. T. Kelley, "Rank-Deficient Nonlinear Least Squares Problems",
MBS workshop on Computational challenges in integrative biological modeling, Columbus, OH, October 2009

C. T. Kelley, "Rank-Deficient Nonlinear Least Squares Problems",
Workshop for the 60th birthday of Prof. E. W. Sachs, Trier, Germany, June 2010

C. T. Kelley, "Rank-Deficient Nonlinear Least Squares Problems",
Sixth East Asia SIAM Conference, Kuala Lumpur, Malaysia, June 2010

C. T. Kelley, "Parallel Computation of Surrogate Models for Potential Energy Surfaces", 2010 International Symposium on Distributed Computing and Applications
to Business, Engineering and Science, Hong Kong, August, 2010

D. M. Mokrauer, "Generating a Feasible Path Between Stable Molecular Geometries with Continuous Steepest Descent" Copper Mountain Conference on Iterative Methods - April 8, 2010 - Copper Mountain, Co.

A. Costolanski, "Efficient Implementation of the Wigner-Poisson Formulation for Modeling a Resonant Tunneling Diode". NANO-DDS Conference, Fort Lauderdale, FL; September 29, 2009.

C. T. Kelley, "Calibration of Ground Water Models and Nonlinear Least Squares",
SIAM Conference on Geosciences, June 2009.

C. T. Kelley, "Calibration of Ground Water Models and Nonlinear Least Squares",
International Conference on Engineering and Computational Mathematics, Hong Kong, China, May 2009.

C. T. Kelley, "Calibration of Ground Water Models and Nonlinear Least Squares",
Oberwolfach Conference on Numerical Methods for Optimization Problems with PDE Constraints, January 2009.

C. T. Kelley, "Pseudo-Transient Continuation", Humboldt University, Berlin, June 2009.

C. T. Kelley, "Deterministic Sampling Methods", AIM Workshop on Derivative-Free Hybrid Optimization Methods for Solving Simulation-Based Problems in Hydrology,
October 2008.

C. T. Kelley, "Pseudo-Transient Continuation", Computer Science and Mathematics Seminar, Oak Ridge National Laboratory, Oak Ridge TN, November 2008.

C. T. Kelley, "Pseudo-Transient Continuation",
First Annual DFG Conference on Optimization with PDE Constraints, Bonn, Germany,October 2007.

C. T. Kelley, "Pseudo-Transient Continuation", Third International Conference of Applied Mathematics, Plovdiv, Bulgaria, August 2007.

Number of Presentations: 25.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Received		Paper
01/11/2013	16.00	A. S. Costolanski, C. T. Kelley, G. W. Howell, A. G. Salinger. An Efficient Parallel Solution of the Wigner Poisson Equation, Proceedings of 21st High Performance Computing Symposium (HPC 2013) (01 2013)
01/31/2010	4.00	A. S. Costolanski, C. T. Kelley. Efficient Solution of the Wigner-Poisson Equation for Modeling Resonant Tunneling Diodes, (01 2010)
02/15/2010	5.00	David Mokrauer, C. T. Kelley, Alexei Bykhovski. Efficient Parallel Computation of Molecular Potential Surfaces for the Study of Light-Induced Transition Dynamics in Multiple Coordinates, (02 2010)
06/29/2010	6.00	D. Mokrauer, C. T. Kelley, A Bykhovski. Parallel Computation of Surrogate Models for Potential Energy Surfaces, Proceedings of The 9th International Symposium on Distributed Computing and Applications To Business, Engineering & Science (06 2010)
07/27/2011	12.00	D. Mokrauer, C. T. Kelley, A. Bykhovski. Simulations of Light-Induced MolecularTransformations in Multiple Dimensions withIncremental Sparse Surrogates, J. Algorithms and Computational Technology (05 2010)
07/29/2007	2.00	C. T. Kelley, L-Z. Liao, L. Qi, M. T. Chu, J. P. Reese, C. Winton. Projected Pseudo-Transient Continuation, (07 2007)
11/23/2011	13.00	C. T. Kelley, L-Z Liao. Explicit Pseudo-Transient Continuation, Pacific Journal of Optimization (11 2011)
12/21/2011	14.00	David Mokrauer, C. T. Kelley. Sparse Interpolatory Reduced-Order Models for Simulation of Light-Induced Molecular Transformations, Optimization Methods and Software (12 2011)
TOTAL:	**8**	

Number of Manuscripts:

Books

Received		Paper
TOTAL:		

Patents Submitted

Patents Awarded

Awards

PI elected Chair of the Board of Trustees: Society for Industrial and Applied Mathematics (S(AM)

PI appointed Editor-in-Chief, SIAM Review, the flagship journal of SIAM

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Anne Costolanski	0.75	
Davie Mokrauer	0.75	
James Nance	0.75	
FTE Equivalent:	**2.25**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Weidong Zhong	0.20
Brian Pappas	0.20
Greg Recine	0.20
Peiji Zhao	0.20
FTE Equivalent:	**0.80**
Total Number:	**4**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Carl T Kelley	0.10	
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME
David Mokrauer
Anne Costolanski
Total Number: **2**

Names of other research staff

NAME PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Report for Army Research Office grant
W911NF-07-1-0112
Simulation of Devices with Molecular Potentials
Reporting period: 04/01/07 – 11/30/13

1 Problems Studied

The objectives of this project were (1) to design, implement, and analyze novel optimization algorithms for generating the coordinate space trajectories of molecules that are undergoing conformational transformations as a result of light-induced excitations and subsequent relaxation processes and (2) to improve the PI's existing Wigner-Poisson code to enable simulations of devices with more complex barrier structures.

In the period of this report the project has supported three Ph. D. students: David Mokrauer, who finished his Ph. D. in 2012, Anne Costolanski, who finished her Ph. D. in 2013, and James Nance.

Publications from the project include a book [16], seven journal papers [5, 14, 17, 18, 27, 29, 30] two Ph. D. theses [4, 31], two articles in refereed proceedings [6, 28], one submitted journal paper [35], and a Sandia technical report [7].

2 Important Results

2.1 Molecular Confirmation and Dynamics

The objective in this part of the project was to design an efficient algorithm for simulation of light-induced molecular transformations. The simulation seeks to follow the relaxation path of a molecule after excitation by light. The simulator is a predictive tool to see if light excitation and subsequent return to the unexcited or ground state will produce a different configuration than the initial one.

We simulate the results of the excitation, rather than the excitation itself. The excitation will change the quantum state of a molecule. Our objective is to design software that will let one explore the possible changes in a molecule after a sequence of excitations.

The goals of the simulation are not only to identify the end point, but to report the entire path in an high-dimensional configuration space so that one can look for nearby paths to interesting configurations and examine the energy landscape near the path to see if low energy barriers make jumping to a different path possible. We will describe the final version of the algorithm from [31]. This version represents an evolution of the ideas from earlier versions of the algorithm [28–30]. The software has also been applied to sensors in [3].

As pointed out in these earlier papers, previous work on this type of problem (see [26, 32, 36], for example) did not address the general simulation issue, but rather were investigations of specific reactions using Gaussian scans of the surface for the particular molecule of interest. We are the first to address the general problem for more than a single degree of freedom. Our approach uses the Smolyak sparse interpolation [34] method to build a surrogate model

of an expensive molecular dynamics code (in our particular case Gaussian [11]), and uses that model to drive a numerical ODE integrator.

We begin in § 2.1.1 with a precise statement of the problem and the stages of model reduction we will need to make a solution computationally tractable.

2.1.1 Background

The task is to develop a design tool which will simulate molecular changes after excitation. Ideally, we would do this by computing the ground state, simulating excitation with a quantum chemistry code (in our case Gaussian [11]), and then following the gradient descent path in molecular configuration space (bond lengths, valence angles, and torsion angles).

Molecules of interest can have hundreds of atoms and degrees of freedom. One cannot vary all of the degrees of freedom at once in a dynamic simulation because the simulator is too computationally costly. Hence, we must apply several layers of model reduction.

The first of these is to isolate a few molecular coordinates of particular interest and vary only those in the dynamic simulation. The simulator computes an energy $\mathcal{E}_\ell(p)$ as a function of a vector of configuration variables (torsion and bond angles) $p \in R^N$ and the quantum state $\ell = 0, 1, \ldots$. We split

$$p = \begin{pmatrix} x \\ \xi \end{pmatrix}$$

into a low-dimensional vector of design variables x and the remainder ξ. Given ℓ, we compute the energy $E_\ell(x)$ as a function of x alone via

$$E_\ell(x) = \min_\xi \mathcal{E}_\ell \begin{pmatrix} x \\ \xi \end{pmatrix} \tag{1}$$

Gaussian approximates the solution of the optimization problem in (1) with a variant of the the BFGS [1,8,9,12,15,33] algorithm. The objective of this project is to simulate excitation of a molecule from one quantum state ℓ to another ℓ' and the subsequent relaxation to a local minimum of $E_{\ell'}$. The simulator will do this repeatedly for a sequence of states, beginning and ending at $\ell = 0$. We seek a sequence of states for which the initial configuration at the ground state ($\ell = 0$) is different from the one at the end of the sequence of excitations.

For each ℓ, we would ideally compute the local minimum with the gradient descent method, *i. e.* integrate the dynamics

$$\dot{x} = -\nabla E_\ell(x) \tag{2}$$

with initial data given either by the ground state configuration (for $\ell = 0$ at the start of the simulation) or by the result of excitation from a local minimum at another state. The evaluation of ∇E_ℓ is too expensive to drive the numerical solution of (2), so we apply a second level of model reduction and replace E_ℓ with a piecewise polynomial interpolant. This is sufficient, if done carefully, to solve simple problems with as many as two degrees of freedom (*i. e.* $\ell \in R^2$), and we report on results with a simple two-dimensional spline interpolation in [28, 29]. The problems with such an interpolation are that the number of

nodes increases exponentially with the number of degrees of freedom (the size of x) and one must take care with the ordering of the evaluation of the nodes to make sure that the internal optimization has a sufficiently good initial iteration. The internal optimization in Gaussian can fail if one does not pay attention to the latter problem.

Our solution to this complexity problem was to use a sparse grid [34] for the interpolation nodes. The size of the grid grows polynomially with the dimension. Moreover the grids for given orders of accuracy are nested, enabling us to perform error estimation and control.

2.1.2 Results

Mokrauer defended his thesis [31] and graduated in August 2012. His research with the PI was the first to use sparse interpolation as a surrogate model for molecular potential energy functionals. This is important as it enables one to remove calls to a quantum chemistry simulator from a dynamic simulation of light-induced molecular transition dynamics. The papers from his thesis [27–30, 30] have all appeared. Mokrauer's LITES code has been used in [3, 27, 30] for simulation of Butene, Stilbene, and Azo-benzene.

The algorithm in the LITES code builds the interpolation adaptively, iterpolating over patches in configuration space as the integration of the dynamics progresses. While this worked well, we are not rethinking that approach as we find ways to interpolate an entire energy landscape with a single interpolation.

The Azo-Benzene simulation encountered difficulties because two energy surfaces intersected. James Nance, the final student on the project, was working on making the evaluation of the sparse interpolant more efficient so we can simultaneously track multiple conformational paths from different initial points.

When the project ended, the PI found new funding for Nance and we hope to continue the work. This will not only be useful in understanding what happens near local maxima after a drop from an excited state to a lower one, but also what happens when a path crosses an intersection of energy surfaces. We must also, of course, devise an efficient and robust approach to detecting intersections. Our first approach at this will be simply to look for a sign change in the difference of energies on the two paths as the integration progresses.

Nance and the PI have made improvements to the algorithms in Mokrauer's work. The simulation is now fast enough to run ensembles of trajectories in configuration space to capture the effects of thermal fluctuations.

2.2 Wigner-Poisson Solver

In § 2.2.1 we will describe the problem and the older work of the PI and others. In § 2.2.2 we will summarize the results obtained in this project.

2.2.1 Background

The Wigner-Poisson equation [37] is an integro-differential equation that models the quantum transport of electrons in a semiconductor device, such as an resonant tunneling diode [2, 10,

38, 39]. The steady-state equation is for the distribution function $f(x,k)$, which depends on space x and momentum k. The steady-state problem is of interest in its own right, and for analysis of dynamic stability of solutions of the time-dependent problem. We write the equation using the notation from [38] as

$$W(f) = Df + P(f) + \left(\frac{\partial f}{\partial t}\right)_{coll} = 0. \tag{3}$$

The linear term Df on the right side of (3) represents the kinetic energy effects on the distribution and is given by

$$Df = -\frac{hk}{2\pi m^*}\frac{\partial f}{\partial x}. \tag{4}$$

In (4), h is Planck's constant and m^* is the effective mass of the electron. The second term, $P(f)$, is the nonlinear term in the equation and accounts for the potential energy effects on the distribution

$$P(f) = -\frac{4}{h}\int_{-K}^{K} f(x,k')T(x,k-k')dk'. \tag{5}$$

The function $T(x,k)$ is defined by

$$T(x,k) = \int_0^{\frac{L_c}{2}} [U(x+y) - U(x-y)]\sin(2yk)dy. \tag{6}$$

In this equation, $U(x)$ is the electric potential as a function of position and L_c is the correlation length. This term is nonlinear in f because $U(x)$ depends on f through Poisson's equation (see (10) and (12)). The last term describes electron-electron scattering

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \frac{1}{\tau}\left[\frac{\int_{-K}^{K} f(x,k')dk'}{\int_{-K}^{K} f_0(x,k')dk'} f_0(x,k) - f(x,k)\right] \tag{7}$$

In (7), τ is the relaxation time, and $f_0(x,k)$ is the equilibrium Wigner distribution. f_0 is the solution of (3) when there is no voltage difference (zero-bias) across the device. The equations for f_0 differ both in form and in analytic properties from those for the nonzero-bias case.

Boundary conditions are imposed at the device edges to describe the distribution of electrons entering the device. On the left ($x = 0$), we have for $k > 0$ (electrons with positive momentum that are moving right)

$$f(0,k) = f(k) \equiv \frac{4\pi m^* k_B T}{h^2}\ln\left(1 + \exp\left[\frac{1}{k_B T}\left(\frac{h^2k^2}{8\pi^2 m^*} - \mu\right)\right]\right). \tag{8}$$

Similarly on the right ($x = L$) we specify f for $k < 0$ (electrons with negative momentum that are moving left)

$$f(L,k) = f(k). \tag{9}$$

In (8) and (9), k_B is Boltzmann's constant, T is the temperature, μ is the Fermi energy at the endpoints. The electric potential $U(x)$ is the sum of the potential barrier $\Delta_c(x)$ that arises

from the heterojunction of the two different semiconductor materials and the electrostatic potential $u(x)$. The electrostatic potential is the solution of Poisson's equation

$$\frac{d^2u}{dx^2} = \frac{q^2}{\epsilon}\left[N_d(x) - \frac{1}{2\pi}\int_{-K}^{K} f(x,k')dk'\right]. \tag{10}$$

In (10), q is the charge of the electron, ϵ is the dielectric constant, and $N_d(x)$ is the doping profile. N_d is piecewise constant, with a small number (≤ 10) of discontinuities. The boundary conditions for (10) are

$$u(0) = 0, u(L) = -V_{bias}, \tag{11}$$

where $V_{bias} \geq 0$ is the applied voltage (bias). The potential U is given by

$$U(x) = u(x) + \Delta_c(x), \tag{12}$$

where $\Delta_c(x)$ is piecewise constant with a small number of discontinuities.

We will assume that the structure is symmetric about $x = \frac{L}{2}$, *i. e.*

$$N_d(x) = N_d(L-x) \text{ and } \Delta_c(x) = \Delta_c(L-x). \tag{13}$$

To evaluate the integral in (6) we must extend U outside of the interval $[0, L]$. We do this by defining $U(x) = U(L)$ for $x > L$ and $U(x) = U(0)$ for $x < 0$. With this definition, U is a piecewise smooth function of x, having discontinuities where Δ_c does. f_0 is the solution to the zero-bias problem ($V_{bias} = 0$), which differs from the nonzero-bias ($V_{bias} > 0$) case in that the collision term is missing from the integro-partial differential equation, resulting in

$$W(f) = Df + P(f) = 0, \tag{14}$$

and $V = 0$ in the boundary conditions (11) for the Poisson equation.

Unlike [38], where the momentum was unbounded, older work [20, 21, 23–25, 40] of the PI and his collaborators limited k. The reasons for this were that the standard discretization [2, 38] has been found to fail to converge as the number of grid points in momentum increases [19], whereas limiting K to a physically reasonable value enable not only numerical observations of convergence, but also a proof [19, 24].

2.2.2 Results

The work in the current project [4–6] began by correcting some errors in the discretizations in the fortran codes. This led to a significant improvement in accuracy [5], which the PI improved further with a grid that was nonuniform in both space and momentum. Costolanski and the PI implemented these ideas in a matlab code. The matlab code was promising enough to motivate us to implement the new discretization in C++ and parallelize the algorithm using the Sandia Trilinos [13] framework.

Costolanski's final C++ code has non-uniform grids in both space and momentum [6]. Costolanski graduated in August 2013. Her thesis reports on numerical to determine the

difference between the discretizations from [10, 38] and those from [22–24], grid refinement studies, stability analysis, and continuation results. Her work corrected several errors in previous simulators and, at least numerically, gave new insights into the dynamic stability of the Wigner-Poisson model.

References

[1] C. G. Broyden, *A new double-rank minimization algorithm*, AMS Notices, 16 (1969), p. 670.

[2] F. A. Buot and K. L. Jensen, *Lattice Weyl-Wigner formulation of exact many-body quantum-transport theory and applications to novel solid-state quantum-based devices*, Phys. Rev. B, 42 (1990), pp. 9429–9457.

[3] A. Byhkovski and D. Woolard, *Physics and modeling of DNA-derivative architectures for long-wavelength bio-sensing*, 2011. to appear in Proceedings of CMOS Emerging Technologies 2011, Whistler, BC, Canada.

[4] A. Costolanski, *Numerical Simulation of Resonant Tunneling Devices Described by the Wigner-Poisson Equations*, PhD thesis, North Carolina State University, Raleigh, North Carolina, 2013.

[5] A. S. Costolanski and C. T. Kelley, *Efficient solution of the wigner-poisson equation for modeling resonant tunneling diodes*, IEEE Transactions on Nanotechnology, 9 (2010), pp. 708–715.

[6] A. S. Costolanski, C. T. Kelley, G. W. Howell, and A. G. Salinger, *An efficient parallel solution to the Wigner-Poisson equations*, in High Performance Computing Symposium (HPC 2013), F. Liu, ed., no. 6 in Simulation Series Vol 45, Society for Modeling & Simulation International, Curran Associates, Inc., April 2013, pp. 773–780.

[7] A. S. Costolanski and A. G. Salinger, *Modeling a resonant tunneling diode using trilinos*, Tech. Rep. SAND2010-3083P, Sandia National Laboratories, 2010.

[8] J. E. Dennis and R. B. Schnabel, *Numerical Methods for Unconstrained Optimization and Nonlinear Equations*, no. 16 in Classics in Applied Mathematics, SIAM, Philadelphia, 1996.

[9] R. Fletcher, *A new approach to variable metric methods*, Comput. J., 13 (1970), pp. 317–322.

[10] W. R. Frensley, *Wigner-function model of a resonant-tunneling semiconductor device*, Phys. Rev. B, 36 (1987), pp. 1570–1580.

[11] M. J. Frisch, A. Frisch, F. R. Clemente, and G. W. Trucks, *Gaussian 09 User's Reference*, Gaussian inc., Wallingford, CT, 2009.

[12] D. Goldfarb, *A family of variable metric methods derived by variational means*, Math. Comp., 24 (1970), pp. 23–26.

[13] M. A. Heroux, R. A. Bartlett, V. E. Howle, R. J. Hoekstra, J. J. Hu, T. G. Kolda, R. B. Lehoucq, K. R. Long, R. P. Pawlowski, E. T. Phipps, A. G. Salinger, H. K. Thornquist, R. S. Tuminaro, J. M. Willenbring, A. Williams, and K. S. Stanley, *An overview of the Trilinos project*, Tech. Rep. 3, Sandia National Laboratories, 2005.

[14] I. C. F. Ipsen, C. T. Kelley, and S. R. Pope, *Nonlinear least squares problems and subset selection*, SIAM J. Numer. Anal., 49 (2011), pp. 1244–1266.

[15] C. T. Kelley, *Iterative Methods for Optimization*, no. 18 in Frontiers in Applied Mathematics, SIAM, Philadelphia, 1999.

[16] ——, *Implicit Filtering*, no. 23 in Software Environments and Tools, SIAM, Philadelphia, 2011.

[17] C. T. Kelley and L.-Z. Liao, *Explicit pseudo-transient continuation*, Pacific Journal of Optimization, 9 (2013), pp. 77–91.

[18] C. T. Kelley, L.-Z. Liao, L. Qi, M. T. Chu, J. P. Reese, and C. Winton, *Projected pseudo-transient continuation*, SIAM J. Numer. Anal., 46 (2008), pp. 3071–3083.

[19] M. S. Lasater, *Numerical Methods for the Wigner-Poisson Equations*, PhD thesis, North Carolina State University, Raleigh, North Carolina, 2005.

[20] M. S. Lasater, C. T. Kelley, A. Salinger, D. L. Woolard, and P. Zhao, *Enhancement of numerical computations of the Wigner-Poisson equations for application to the simulation of THz-frequency RTD oscillators*, in Proceedings of SPIE: Chemical and Biological Standoff Detection II Volume 5584, paper number 07, J. O. Jensen and J.-M. Theriault, eds., 2004, pp. 42–51.

[21] ——, *Parallel solution of the Wigner-Poisson equations for RTDs*, in 2004 International Symposium on Distributed Computing and Applications to Business, Engineering and Science, Q. Qingping, ed., Wuhan, China, 2004, Hubei Science and Technology Press, pp. 672–676.

[22] ——, *Parallel parameter study of the Wigner-Poisson equations for RTDs*, Computers and Mathematics with Applications, 51 (2006), pp. 1677–1688.

[23] M. S. Lasater, C. T. Kelley, A. Salinger, P. Zhao, and D. L. Woolard, *Simulating nanoscale devices*, International Journal of High Speed Electronics and Systems, 16 (2006), pp. 677–690.

[24] M. S. Lasater, C. T. Kelley, A. G. Salinger, D. L. Woolard, G. Recine, and P. Zhao, *Analysis of a scalable preconditioner for the Wigner-Poisson equation*, International Journal of Pure and Applied Mathematics, 37 (2007), pp. 247–270.

[25] M. S. Lasater, C. T. Kelley, P. Zhao, and D. L. Woolard, *Numerical tools for the study of instabilities within the positive-differential-resistance regions of tunnelling devices*, in Proceedings of 2003 3nd IEEE Conference on Nanotechnology, San Francisco, CA, August 12–14, 2003, IEEE, 2003, pp. 390–393.

[26] Y. Luo, B. Gelmont, and D. Woolard, *Bio-molecular devices for terahertz frequency sensing*, in Molecular and Nano Electronics: Analysis, Design, and Simulation, J. Seminario, ed., 2007, pp. 55–81.

[27] D. Mokrauer and C. T. Kelley, *Sparse interpolatory reduced-order models for simulation of light-induced molecular transformations*, Opt. Meth. Software, (2012). 10 pages, doi = 10.1080/10556788.2012.693928.

[28] D. Mokrauer, C. T. Kelley, and A. Bykhovski, *Parallel computation of surrogate models for potential energy surfaces*, in 2010 International Symposium on Distributed Computing and Applications to Business, Engineering and Science, Q. Qingping and G. Yucheng, eds., Los Alamitos, CA, 2010, IEEE, pp. 1–4.

[29] ——, *Efficient parallel computation of molecular potential surfaces for the study of light-induced transition dynamics in multiple coordinates*, IEEE Transactions on Nanotechnology, 10 (2011), pp. 70–74.

[30] ——, *Simulations of light-induced molecular transformations in multiple dimensions with incremental sparse surrogates*, J. Algorithms and Computational Technology, 6 (2012), pp. 577–592.

[31] D. M. Mokrauer, *Interpolatory Surrogate Models for Light-Induced Transition Dynamics*, PhD thesis, North Carolina State University, Raleigh, North Carolina, 2012.

[32] I. J. Palmer, I. N. Ragazos, F. Bemardi, M. Olivucci, and M. A. Robb, *An mc-scf study of the s1 and s2 photochemical reactions of benzene*, J. Am. Chem. Soc., (1993), pp. 673–682.

[33] D. F. Shanno, *Conditioning of quasi-Newton methods for function minimization*, Math. Comp., 24 (1970), pp. 647–657.

[34] S. Smolyak, *Quadrature and interpolation formulas for tensor products of certain classes of functions*, Soviet Math. Dokl., 4 (1963), pp. 240–243.

[35] A. Toth and C. T. Kelley, *Convergence analysis for anderson acceleration*, 2013. Submitted for publication.

[36] C. Van Caillie and R. D. Amos, *Geometric derivatives of density functional theory excitation energies using gradient-corrected functionals*, Chem. Phys. Letters, 317 (2000).

[37] E. Wigner, *On the quantum correction for thermodynamic equilibrium*, Phys. Rev., 40 (1932), pp. 749–759.

[38] P. Zhao, H. L. Cui, and D. L. Woolard, *Dynamical instabilities and I-V characteristics in resonant tunneling through double barrier quantum well systems*, Phys. Rev. B, 63 (2001), p. 75302.

[39] P. Zhao and D. L. Woolard, *A multi-subband theoretical criterion for the design of a double-barrier quantum-well intrinsic oscillator*. United States Patent Application.

[40] P. Zhao, D. L. Woolard, M. S. Lasater, and C. T. Kelley, *Terahertz-frequency quantum oscillator operating in the positive differential resistance region*, in Proceedings of SPIE Defense and Security Symposium 2005: Terahertz for Military & Security Application III, paper number 5790-34, vol. 5790, 2005, pp. 289–300.